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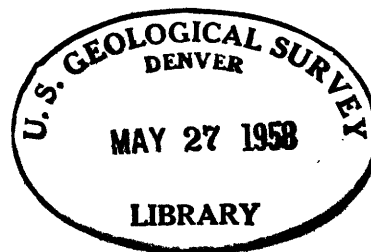This document consists of 42   pages.
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VANADIUM AND URANIUM IN ROCKS AND ORE DEPOSITS

By

R. P. Fischer

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VANADIUM AND URANIUM IN ROCKS AND ORE DEPOSITS

By R. P. Fischer

ABSTRACT

Trace amounts of vanadium and uranium are common in both igneous and sedimentary rocks. Vanadium is more abundant in mafic igneous rocks, uranium in silicic ones. Both metals tend to concentrate in some sedimentary rocks containing organic material.

Uranium accumulates in some igneous rocks, pegmatites, veins, sandstones, limestones, conglomerates, coals, black shales, and phosphorites, but the more productive deposits are those in veins, sandstones, and conglomerates. Uranium minerals have been recognized in many types of hydrothermal veins.

Productive sources of vanadium include deposits with uranium in sedimentary rocks, iron ores (both magmatic and sedimentary), vanadates of base metals, asphaltic deposits, phosphate rock, and the soot or ash of some natural carbonaceous material. None of these deposits are clearly of hydrothermal origin. Accessory vanadium minerals are not generally recognized in hydrothermal deposits except titanium-bearing veins and gold-telluride deposits.

The average vanadium content of 775 samples of ores and mill products is less than 100 parts per million (ppm), which is less than the average reported for igneous rocks and shales. A group of 296 samples from uranium-bearing veins also shows less than 100 ppm V.

These data suggest that vanadium does not tend to concentrate in the common hydrothermal environment, and specifically that it does not concentrate in most veins containing uranium ore. If this is true, evidence of unusual processes and conditions might be required to explain the origin and source of vanadium and uranium in deposits containing commercial amounts of both metals.

INTRODUCTION

Vanadium and uranium are intimately associated in many productive uranium deposits in sedimentary rocks, especially in those of the type found in sandstone. The genesis of these deposits is an unsolved problem and the source of the metals is also unknown. This study of vanadium and uranium in rocks and ore deposits was undertaken to see if the geochemical habits of these metals might focus attention on certain aspects of the problems of genesis and source of metals that need special study.

It has long been known that vanadium and uranium are disseminated in igneous rocks but are not closely associated in this environment, whereas, these two metals do get together in the sedimentary environment, especially in rocks containing organic material. On these aspects of the subject, this report merely summarizes information available in published literature. It has also long been recognized that vanadium and uranium do not commonly concentrate together in normal hydrothermal deposits, but heretofore, this picture has been based largely on negative information-- the lack of known occurrences. Some quantitative information on the amount of vanadium in ore deposits is contributed in this report.

GEOCHEMICAL CHARACTERISTICS OF VANADIUM AND URANIUM

The information in this section is summarized mainly from the recent comprehensive studies on geochemistry by Rankama and Sahama (1950) and by Goldschmidt (1954). The reader interested in more detailed information should refer to these works and the references cited in them.

In igneous rocks

Vanadium is relatively abundant among the "trace elements" in igneous rocks. It averages 150 grams per metric ton (parts per million), is slightly more abundant than zinc, about twice as abundant as copper, and about 10 times more abundant than lead. Uranium averages 4 parts per million (ppm) in igneous rocks (Rankama and Sahama, 1950, table 2, 3, p. 39 and 40).

Both vanadium and uranium are classed among the "lithophile" elements, those that are enriched in the silicate crust. Within this environment, however, the two metals are not intimately associated.

Vanadium is more abundant in the mafic igneous rocks than in the silicic ones. Vanadium does not form a constituent part of any common rock-forming mineral; rather its ions replace those of iron and aluminum in the common ferro-magnesian minerals and those of titanium and iron in titanium minerals and titaniferous iron ores.

Uranium, on the other hand, concentrates more abundantly in the later or more silicic part of igneous differentiates. In these rocks some uranium is held in accessory minerals, such as zircon, monazite, and allanite, and some is in a loosely bound form in mineral interstices

(McKelvey, Everhart, and Garrels, in press). Uranium is common in pegmatites and hydrothermal veins; many uranium minerals are found in pegmatites and veins, but uraninite is the most important of these.

On weathering

During weathering of igneous rocks, much of the vanadium goes into clay minerals. Some of it, and perhaps a large part of it, must remain with these minerals as they are transported to places where they accumulate as sedimentary rocks, for argillaceous sediments are generally richer in vanadium than sandstone or limestone. Some vanadium, however, goes into solution, from which it can enter the geologically temporary states of combination with heavy metals to form vanadates or be taken by plants and animals. Apparently, of the vanadium that reaches the sea in solution, not much remains in solution, for only 0.0003 ppm is present in sea water whereas 90 ppm is supplied to sea water (Rankama and Sahama, 1950, table 6.19, p. 295).

The habits of uranium during weathering are more varied. Some of the uranium-bearing minerals in rocks and veins are refractory, and they mainly weather mechanically and are distributed to clastic sediments. Other minerals oxidize readily to form complex secondary minerals and soluble salts; these salts are carried seaward, either in solution or adsorbed on hydroxide gels—Rankama and Sahama (1950, table 6.19, p. 295) report that 0.0016 ppm U is present in sea water whereas 0.6 ppm is supplied to sea water.

In sedimentary rocks

The average content of vanadium is <10 ppm in carbonate rocks,
20 ppm in sandstone, and 120 ppm in clays and shales (Rankama and Sahama,
1950, table 5.52, p. 226). Shaw (1954, table 4, p. 1170) also shows a
120 ppm vanadium content in shales, schists, and gneisses. As a general
rule, vanadium increases with the increase in argillaceous material and
especially with an increase in organic matter; it is richly concentrated
in some coal, petroleum, and asphalt (Jost, 1932). Uranium is more
dispersed and of uniform grade in the three principal types of sedi-
mentary rocks. Rankama and Sahama (1950, table 5.52, p. 226) give 1.2
ppm U in sandstones, 1.2 ppm in shales, and 1.3 ppm in limestones. These
authors show (p. 637), however, that uranium is significantly concentrated
in some carbonaceous shales of marine origin, in certain coals, and in
some petroleum, as in vanadium. Erickson, Myers, and Horr (1954) give
more specific information regarding uranium and vanadium, as well as
other metals, in crude oil, asphalt, and petroliferous rock.

URANIUM DEPOSITS

Uranium is widely distributed and its types of occurrences much varied;
it is enriched in some igneous rocks, pegmatites, veins, sandstones, lime-
stones, conglomerates, coals, black shales, and phosphorites (McKelvey,
Everhart, and Garrels, in press). Representatives of many of these types
have yielded production, either for uranium itself or as a byproduct, but
the deposits in veins, sandstones, and conglomerates have been the more
productive.

Veins

As Everhart and Wright (1953) have recently summarized the geologic character of typical uranium-bearing (pitchblende) veins, including the more productive deposits, only the general features of these deposits will be mentioned here. They recognize two major types of deposits. One, a nickel-cobalt-native silver type, has a complex mineralogy, a gangue dominantly of carbonates with lesser silica, and occurs in metasediments and volcanic host rocks. The second, a siliceous-pyrite-galena type, has a simple mineralogy, a gangue of silica and fluorite with lesser carbonate, and occurs in felsic intrusives. McKelvey, Everhart, and Garrels (in press) have added a third type, iron-titanium veins, in which uranium occurs as the mineral davidite, with a silica gangue, in granitic intrusives.

Intensive exploration for radioactive material during recent years has revealed the presence of uranium in many vein deposits of varied metal and mineral assemblages. Many of these deposits, however, have not yielded significant production, because the uranium content is low or is restricted to small ore shoots.

Generally speaking, all of these deposits have characteristics of typical veins, to which an origin of hydrothermal mineralization from a hypogene source is normally ascribed.

Sandstone deposits of the Colorado Plateau

The so-called "carnotite" deposits of the Colorado Plateau form a group of deposits with wide distribution and many common characteristics. They have yielded important amounts of vanadium, uranium, and radium.

Although these deposits are found in many formations, ranging from late Paleozoic to middle Tertiary in age, the more productive deposits are restricted to a few stratigraphic units of Mesozoic age. Most of the deposits are in sandstone beds of continental origin, though some are in limestone and a few in shale. The host rocks in nearly all deposits contain carbonaceous material, mostly fossil wood.

The early minerals in the ore consist of low-valent oxides and silicates of vanadium and uranium, small amounts of copper and iron sulfides, and traces of galena and sphalerite. The ore minerals alter to higher valent oxides of vanadium and to vanadates and other secondary uranium minerals. They mainly occupy pore spaces in the sandstone, though in part they replace sand grains and associated argillaceous and carbonaceous material. The ore bodies are tabular layers that lie nearly parallel to bedding but do not follow beds in detail. Most ore bodies are small, and they range from masses only a few feet across to those several hundred feet across.

It is generally agreed that the ore minerals were introduced into their present position by solutions, but the nature of these solutions and the source of the metals are not known. Some students believe the solutions were hypogene and that the metals were intro-duced from deep-seated sources; others favor the idea that the metals were originally disseminated in the ore-bearing and associated rocks and were transported and concentrated at favorable sites by aqueous solutions or perhaps even petroleum. It is also generally agreed that sedimentary structures, such as lenses, had some influence on the migration of the ore-bearing solutions and the localization of many ore deposits. In addition, the regional distribution of deposits suggests to some geologists that regional deformation also influenced localization by providing pathways for the vertical movement of solutions to ore-bearing beds, and a few deposits show a close association with such vertical pathways. Igneous activity and mineralization of definite hydrothermal origin are not closely associated with carnotite deposits, except in a few places.

McKelvey, Everhart, and Garrels (in press) give a fairly complete list of references to reports on these deposits.

Deposits similar to these on the Colorado Plateau are also present elsewhere; some in Wyoming and South Dakota have yielded significant production.

Limestone deposits of Tyuya Muyan, Russia

At Tyuya Muyan, Fergana, in central Asia, oxidized uranium, vanadium,
and copper minerals, associated with barite, calcite, and quartz, occur
in limestone. The ore bodies are peculiar pipelike structures that
partly fill cavities and perhaps partly replace the host rock. The area
is one of complex structure and geologic history, with considereable
faulting and igneous activity.

The origin of these deposits, also, is in doubt. Pavlenko (1933)
believes the ore formed from thermal solutions derived from diabase
intrusives. According to Bain (1950, p. 295), Fersman considers the
uranium and vanadium to have been leached from nearby black shales,
which, according to Rankama and Sahama (1950, p. 638) contain" approxi-
mately 400 g/ton U and 850 g/ton V."

Witwatersrand conglomerate

Conglomerate beds of the Witwatersrand, South Africa, are
yielding large quantities of uranium as well as gold. In addition to
native gold, the ore minerals consist of uraninite and thucholite, a
uraninite-hydrocarbon aggregate. These minerals, along with minor
amounts of common sulfides are mainly disseminated in pore spaces in
lenses of coarse sandstone and conglomerate. Some gold and uranium,
but apparently only minor amounts, occur in quartz and thucholite
veinlets where these cross ore-bearing beds. Although the rocks are
fractured and also invaded by igneous dikes, the ore bodies are not
clearly localized by these features. A "placer" versus "hydrothermal"

origin for the gold ores has long been debated among geologists and the

same discussion continues since the discovery of uranium in these

deposits. Readers interested in more detail regarding these deposits

and the problem of their origin are referred to McKelvey, Everhart, and

Garrels (in press) and the reports they list.

VANADIUM IN ORE DEPOSITS

There are but few deposits in which vanadium alone is sufficiently

concentrated to support a profitable operation, though there are several

types of deposits that have yielded byproduct vanadium or from which

production might be economic under reasonably favorable conditions.

These are described below under "Productive vanadium deposits." Vanadium

shows little or no tendency to concentrate in most types of ore deposits;

available information regarding the vanadium content of these deposits

is presented in the section entitled, "Vanadium in other deposits."

Productive vanadium deposits

Vanadium-uranium deposits in sandstone and limestone

A description of the vanadium-uranium deposits in sandstone on

the Colorado Plateau and in limestone at Tyuya Muyan, Russia, has been

given previously.

Iron ores

Many iron ores contain small amounts of vanadium, and some have

yielded byproduct vanadium. Commonly the titaniferous-magnetite deposits

are the most vanadiferous (Singewald, 1913); the vanadium content ranges

from about 0.1 percent V to more than 1 percent and probably averages between 0.3 and 0.5 percent. In these deposits, vanadium is reported to be in the magnetite rather than in the titanium minerals (Balsley, 1943), a seemingly peculiar relation considering that most nontitaniferous magnetites contain less vanadium.

Many sedimentary iron ores contain 0.01 to 0.1 percent V. During World War II Germany produced considerable vanadium from iron ores containing about 0.1 percent V (Fischer, 1946). Vanadium is also concentrated in laterites and bauxites, especially those derived from mafic igneous rocks.

Vanadate ores

Vanadates of lead, zinc, and copper are found in many base-metal deposits in southwestern United States, Mexico, South America, Spain, Africa, and Australia; some vanadium has been produced from a number of these deposits, but the most productive are those at Broken Hill, Northern Rhodesia, and in the Otavi district, Southwest Africa. Most, though not all, of these deposits are in carbonate country rock. Typically they are in areas of moderately arid climate and deep oxidation; the vanadate ores are said to be in the oxidized parts of the deposits.

Evidence and opinions differ as to the source of the vanadium in these deposits. Skerl (1934) reports that the unoxidized ore at Broken Hill was tested chemically and spectrographically, but no trace of vanadium was found; Clark (1931) states that the primary ores in Southwest Africa contain little or no vanadium and believes that no reasonable amount of concentration from the weathering of eroded lead-zinc ore bodies could

account for the vanadium ore. In both areas the vanadium is thought to have come from that originally disseminated in the surrounding rock. The same explanation has been offered for other deposits.

In contrast to the evidence and opinions mentioned above, Peterson (1938) finds that the vanadate minerals at the Mammoth-St. Anthony area, Arizona, were introduced during the last stage of hypogene mineralization and later than the base-metal sulfides.

In addition, Newhouse (1934), aided by spectroscopic work of Claussen (1934), tested specimens of pyrite, galena, and sphalerite for vanadium and concluded that at least some of the vanadium in the vanadates of the oxidized base-metal deposits was derived from the trace amounts in the sulfides. Five selected samples each of pyrite, galena, and sphalerite were tested; 1 sample of pyrite and 5 of galena showed $0.0n - 0.00n$ percent V spectrographically, and the vanadium content of the other samples was below the limit of detection. One pyrite sample showed 0.01 percent V by chemical analysis and the rest much less; the sphalerite samples showed less vanadium than the pyrite samples; and the chemical tests on the galena samples showed a few thousandths percent, confirming the spectroscopic results (Newhouse, 1934).

Moritz (1933) reported about 0.001 percent vanadium in the sulfide ore (tennantite, enargite, sphalerite, and other sulfides), as well as in calcite and dolomite, and as much as 0.01 percent vanadium in pyrite in the Tsumeb mine, Otavi district, Southwest Africa.

The problem of the origin of the vanadate ore in oxidized base-metal deposits, per se, is not of immediate concern. The source of vanadium may be the country rock, as some believe; or it may be the trace amounts

disseminated in sulfides, as suggested by Newhouse; or it may be a separate

hypogene stage, as reported by Peterson at the Mammoth-St. Anthony deposit.

But two points are of immediate interest; 1) all available evidence shows

only a very low concentration of vanadium in the primary sulfides, and

2) even if the vanadate ore at the Mammoth-St. Anthony area is hypogene, as

Peterson suggests, it is a phase separate from the normal sulfide

mineralization.

Minasragra, Peru

The vanadium sulfide (patronite) deposit at Minasragra, Peru

(Hewett, 1909), has been the most productive single deposit of vanadium.

The ore consists of quisqueite (a hydrocarbon), coke, and patronite;

bravoite, an iron-nickel sulfide, is present in small amounts in the

patronite. These materials occupy a fracture and permeate the adjoining

shale, forming a lens-shaped body up to 30 feet wide and a few hundred

feet long. The fracture dips steeply and crosses bedding at a moderate

angle. Country rock consists of shales and thin-bedded limestones of

Cretaceous age. These rocks are invaded by several igneous dikes and cut

by numerous faults near the deposit.

Similar vanadiferous asphaltic veins are common in this part of

Peru; though none are nearly as rich in vanadium as the Minasragra deposit,

they do contain about 1 percent vanadic oxide. All these asphaltic deposits

apparently are in the same group of sedimentary beds, which also contain

vanadiferous black shales.

Although the origin of the Minasraga deposit certainly is not known, most authorities (Hewett, 1909; Jost, 1932; and Rankama and Sahama, 1950) relate the formation of this deposit to the process responsible for forming asphaltite and its common contamination by vanadium. Thermal solutions, however, may have played a part in transporting or altering the asphaltite and enriching this deposit.

Miscellaneous deposits

Under peculiarly favorable conditions, vanadium has been, or can be, recovered as a byproduct from several other sources. Among these are ash or soot from crude oil or petroleum refinery products or from other carbonaceous material such as natural asphalt and vanadiferous coals. Byproduct vanadium has also been obtained from phosphate rock at Conda, Idaho (Argall, 1943, p.47 and 48); uranium is also present (McKelvey and Nelson, 1950, p. 41). Lovering and Goddard (1950, p. 234) report that in 1910 some gold-telluride ore was shipped for its vanadium content from the Keklonga claim, Boulder County, Colo. A brief discussion of vanadium in gold-telluride veins is given on page 28.

Vanadium in other deposits

Not much information is available regarding the distribution and amount of many elements that occur in ore deposits in quantities below levels of economic value, especially if the elements do not form constituent parts of readily recognized minerals. Vanadium is one of these. The failure of observers and analysts to detect, or mention, the presence of vanadium in many hydrothermal ore deposits can be used, in a negative

manner, to suggest a low vanadium content, as well as to indicate that its geochemical habits do not favor concentration in this particular environment. Even so, conclusions based on such negative information are unsatisfactory. In recent years, however, some quantitative information has become available, and perhaps this information can support broad generalizations.

Vanadium in rocks, ores, and mill and smelter products

In 1942, at the request of the War Production Board, the Geological Survey began a search for certain strategic and minor elements in domestic rocks, ores, concentrates, tailings, smelter slags, and flue dusts. Several hundred samples of these materials were collected by geologists or furnished by mining and smelting companies and were tested for 22 elements, including vanadium, by semiquantitative spectrographic analyses. The analytical results are published in a report by Kaiser, Herring, and Rabbitt (1954).

Although these samples are not completely representative of any single deposit or type of deposit, they give a coverage of most types of ore deposits in the United States—the samples are from deposits that yielded 85 percent or more of the 1942 domestic production of copper, lead, zinc, manganese, mercury, tin, tungsten, and chromium, and lesser percentages of production of aluminum, gold, silver, iron, and pegmatite minerals. As such, these samples have some value on which to base generalizations. Information regarding vanadium in these deposits is summarized below. Similar information regarding vanadium in veins that have been studied and sampled because they are uranium-bearing (or might be), is summarized in the section "Vanadium in uranium-bearing veins."

The semiquantitative spectrographic results for vanadium in rocks, ores, and mill and smelter products (Kaiser, Herring, and Rabbitt, 1954) are mostly expressed in numerical percentages and as V_2O_5. For this study, these values were converted to percent V, and then grouped into the grade classes shown on figure 1, 2, and 3, and table 1 so the values would be more nearly comparable to the manner in which semiquantitative spectrographic results are now being reported by the Geological Survey laboratory. To convert the numerical values of V_2O_5 to V, the figures were multiplied by 0.5 rather than by the true conversion factor of 0.56. Obviously this introduced a consistent error, though one so small as to be of little import, and the error is lost in most cases in conversion to the X catagories.

A few values of V_2O_5 are reported by Kaiser, Herring and Rabbitt (1954) and "X" to the proper decimal place. These were assumed to have a medial value of 5 to the same decimal place, and they were converted in the manner described above. Values reported as 0.001 percent V_2O_5, and those shown as "trace" V_2O_5, are grouped in the category of "trace" V in table 1.

The distribution by grade classes of the 775 samples tested for vanadium is shown in the left side of table 1. The samples were divided into two groups: one group (column 1) includes mill heads, tailings, and ore (including grab samples), as it was thought these might be more representative of ore deposits; the other group (column 2) includes concentrates, slag, and flue dust. There appears to be no significant difference between the two groups. The combined total of these two groups is shown in column 3. The graphic plot below each column shows the distribution of samples in each grade class by percent of the total number of samples.

Table 1. Distribution of vanadium samples by grade classes.

Grade class, percent V_/	Vanadium in some rocks, ores, and mill and smelter products						Vanadium in uranium-bearing veins					
	Column 1 Samples of ore, mill heads, and tails		Column 2 Samples of concentrates, flue dust, and slag		Column 3 Combined total		Column 4 Samples containing 0.01 percent or more U		Column 5 Samples containing <0.01 percent U		Column 6 Combined total	
	Number of samples	Percent of total	Number of samples	Percent of total	Number of samples	Percent of total	Number of samples	Percent of total	Number of samples	Percent of total	Number of samples	Percent of total
0	28	7	30	9	58	7	4	3	2	1	6	2
Trace	15	3	33	9	48	6	3	2	2	1	5	2
.000X$^+$	--	--	--	--	--	--	9	6	21	14	30	10
.00X$^-$	87	21	69	20	156	20	23	16	38	25	61	20
.00X	79	19	84	24	163	21	53	37	49	32	102	35
.00X$^+$	80	19	48	14	128	17	30	21	24	16	54	18
.0X$^-$	86	20	38	11	124	16	8	6	7	5	15	5
.0X	33	8	31	9	64	8	14	10	9	6	23	8
.0X$^+$	8	2	9	3	17	2	--	--	--	--	--	--
.X$^-$	6	1	7	2	13	2	--	--	--	--	--	--
.X	2	0	2	1	4	1	--	--	--	--	--	--
Totals	424	100	351	102	775	100	144	101	152	100	296	100

_/ The limits of the grade classes are generated by integral powers of the cube root of 10 (2.154); for example, .0X$^-$ = 0.01 to 0.0215 percent, .0X = 0.0215 to 0.0464 percent, and .0X$^+$ = 0.0464 to 0.1 percent.

Grade classes expressed in ppm V

Grade classes expressed in percent V
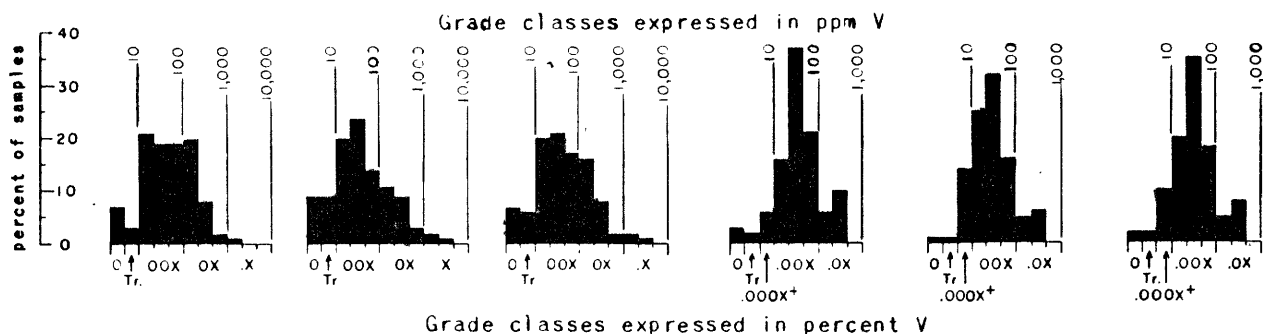
By inspection of the subcolumns "percent of total," it is obvious
that at least half of the total samples in columns 1, 2, and 3 fall in
the grade classes containing .00X or less (0.0046 percent, or 46 ppm,
V or less). At least half of the samples, therefore, contain considerably
less vanadium than the figures given by Rankama and Sahama (1950, table
5.52, p. 226) as V content of igneous rock (150 ppm) or shale (120 ppm);
on the other hand, more than half of the samples contain more than the
average amount of vanadium in sandstone (20 ppm) and limestone (<10 ppm).

Thus, if these 775 samples should be considered representative of
ore deposits in general, it appears that vanadium does not tend to con-
centrate in most deposits; rather, the vanadium content of most samples
possibly represents the vanadium content of the host rock.

For those readers who may be interested in seeing the character
and source of the higher grade vanadium samples reported by Kaiser,
Herring, and Rabbitt (1954), this information is listed in table 2 for
all samples reported to contain 0.1 percent V_2O_5 or more (about 0.056
percent V, or in the .0X[†] class or higher).

Table 2 shows moderate amounts of vanadium in iron, chromium, and
manganese ores, as might be expected. It also shows moderate amounts of
vanadium in samples of some ores of titanium and gold, a relation that
seemed to the writer to be worthy of a sideline investigation and to
justify a brief mention here.

The habits of vanadium to accumulate in magmatic titaniferous
magnetite deposits is well known. The relatively high vanadium content
in brookite and rutile samples (see table 2, samples ARK-26-1, -26-2,

and -26-3; more data regarding vanadium and titanium at Magnet Cove, Ark.,
is given by Fryklund, Harner, and Kaiser, 1954) suggests that the associ-
ation of vanadium with titanium may even extend into other types of
titanium deposits, including titanium-bearing hydrothermal veins. If
this is true, it may explain the presence of vanadium in the deposit of
davidite (uranium-bearing iron-titanium oxide) at Radium Hill, South
Australia (Parkin and Glasson, 1954), as well as the vanadium in the lower
levels of the Ace mine, Saskatchawan, Canada, where ilmenite also is
reported to be abundant (Robinson, 1955, p. 22-23). Only field study
will establish whether the vanadium in these two deposits is more inti-
mately associated with uranium or titanium, or largely independent of
each.

Table 2. Character and source of samples reported by

Kaiser, Herring, and Rabbitt (1954) to contain

0.1 percent V_2O_5 or more.

Percent V_2O_5	Sample number	Character and source of sample
0.1	ARI-7-14	Copper tails, Oracle, Pima County, Ariz.
0.1	ARI-13-13	Molybdenum-vanadium-lead-zinc tailings, Mammoth-St. Anthony mill, Pinal County, Ariz.
0.2	ARK-15-1	Manganese ore, grab sample from high-grade stockpile Batesville district, Arkansas
0.1	ARK-15-2	Manganese ore, grab samples from MRC stockpile, Batesville district, Arkansas
0.1	ARK-15-3	Manganese ore, grab sample from high-grade stockpile, Batesville district, Arkansas
0.1	ARK-15-4	Manganese ore, grab sample from low-grade stockpile, Batesville district, Arkansas
0.58	ARK-26-1	Brookite crystals, composite sample, Magnet Cove, Ark.
0.54	ARK-26-2	Rutile crystals, composite sample, Magnet Cove, Ark.
0.2	ARK-26-3	Rutile concentrate, high grade, Magnet Cove, Ark.
0.1	COL-10-8	Gold concentrates, ore chiefly from Cripple Creek district, Colorado
0.1	COL-10-9	Gold mill heads, ore chiefly from Cripple Creek district, Colorado

Table 2. Character and source of samples reported by

Kaiser, Herring, and Rabbitt (1954) to contain

0.1 percent V_2O_5, or more--Continued.

Percent V_2O_5	Sample number	Character and source of sample
0.6	COL-10-12	Gold refinery byproduct from treated slag, ore chiefly from Cripple Creek district, Colorado
0.6	COL-10-13	Gold refinery slag from roaster, ore chiefly from Cripple Creek district, Colorado
.X	MIC-7-1	Copper concentrates, Kearsarge Amygdaloid mine, Houghton County, Mich. (.X TiO_2)
.X	MIC-7-2	Copper concentrates, Iroquois mine, Houghton County, Mich. (.X TiO_2)
.X	MIC-7-3	Copper concentrates, Allouez No. 3 mine, Houghton County, Mich. (.X TiO_2)
.X	MIC-7-11	Copper concentrates, White Pine mine, Ontonagon County, Mich. (3.6 TiO_2)
.X	MIC-7-12	Copper concentrates, White Pine mine, Ontonagon County, Mich. (.X TiO_2)
0.2	MON-10-25	Gold tailings from tailings dump, Little Ben mine, Phillips County, Mont.
0.1	NEV-27-12	Tungsten tailings, Rawhide, Nev.
0.2	ORE-5-1	Chromite heads, mill sample, ore from Lagoons gold tailings deposits, Coos County, Ore.

Table 2. Character and source of samples reported by

Kaiser, Herring, and Rabbitt (1954) to contain

0.1 percent V_2O_5 or more—Continued.

Percent V_2O_5	Sample number	Character and source of samples
0.4	ORE-5-2	Chromite concentrate, ore from lagoons gold tailings deposit, Coos County, Ore.
0.1	ORE-5-5	Chromite heads, mill sample, Seven Devils mine, Coos County, Ore.
0.2	ORE-5-6	Chromite concentrate, Seven Devils mine, Coos County, Ore.
0.2	ORE-5-8	Chromite mill heads, Coos County, Ore.
0.2	ORE-5-9	Chromite flotation concentrate, Coos County, Ore.
0.2	ORE-5-10	Primary chromite concentrates, Coos County, Ore.
0.1	SD-10-6	Gold heads, Maitland mine, Lawrence County, S. Dak.
0.3	UT-12-2	Grab sample, magnetite iron ore, Iron Mountain mine, Iron County, Utah
0.2	UT-12-3	Magnetite iron ore, Great Western ore body, Iron County, Utah
0.3	UT-12-5	Flue dust from steel plant, Provo, Utah; ore from Iron Mountain mine, Iron County, Utah

Table 2. Character and source of samples reported by

Kaiser, Herring, and Rabbitt (1954) to contain

0.1 percent V_2O_5 or more--Continued.

Percent V_2O_5	Sample number	Character and source of sample
0.1	VA-10-1	Gold tailings, ore from Red Bank Gold mine, Virgilina district, Virginia
0.1	VA-15-1	Manganese concentrates, Appalachian district, Virginia
0.1	VA-15-2	Manganese concentrates, Appalachian district, Virginia
0.2	VA-70-1	Kyanite concentrate, Pamplin, Va.
0.1	WAS-5-1	Heavy sand concentrate (chromite), Cle Elum district, Kittitas County, Wash.

More information regarding the association of vanadium and titanium in uranium-bearing veins is given later in this report.

The presence of roscoelite, the vanadium mica, in gold-telluride veins is not infrequent and suggests a second type of hydrothermal deposit in which vanadium tends to concentrate.

Eckel (1949, p. 74) emphasizes the association of roscoelite with gold-telluride veins in the La Plata district, Colorado. Lovering and Goddard (1950) mention the presence of roscoelite in several veins in the Colorado Front Range, all but one of which are classified as gold-telluride veins. Roscoelite is also mentioned in other reports in districts where gold-telluride deposits are known, but the literature studied by the writer is not sufficiently specific to determine whether or not roscoelite and the telluride minerals are closely associated.

The specific association of vanadium with gold tellurides was noted by de Launay (1911), whereas Lindgren (1933, p. 873) generalized, stating "Roscoelite is found in many gold-quartz veins." This subject is introduced here merely to call this problem to the attention of geologists, in the hope that others may furnish a better understanding of relations.

Vanadium in uranium-bearing veins

Uranium-bearing (pitchblende or uraninite) veins have been the
source of much of the world's radium and uranium. The geologic
characteristics of the typical and more productive deposits of the
class have been summarized by Everhart and Wright (1953). This
summary makes no mention of vanadium in any of the 13 deposits described,
and both Everhart and Wright have told the writer personally that they
watched for but failed to find mention of vanadium in these deposits in
the geologic reports to which they referred during their study.

In a similar study, Bain (1950) summarized the geologic charac-
teristics of all types of uranium deposits that have been or might be
productive. He classified the deposits as primary or hypogene, sedi-
mentary or bedded, and oxidized. In the primary or hypogene class Bain
mentioned most of the deposits described by Everhart and Wright, as
well as a few other deposits of this type. Again no mention was made
of vanadium in these deposits, though vandium was frequently mentioned
in connection with the descriptions of sedimentary and oxidized deposits.

To obtain quantitative data on vanadium in uranium-bearing veins,
the writer has made a search of published and unpublished material in the
files of the Atomic Energy Commission and the Geological Survey. These data
are presented below, grouped in two categories—geologic samples and ore
samples—because of differences in the character of the samples and in
the methods of assay.

The assay results of the group of "geologic samples" are plotted
on the right side of table 1 and on figure 1. They consist of 296 samples
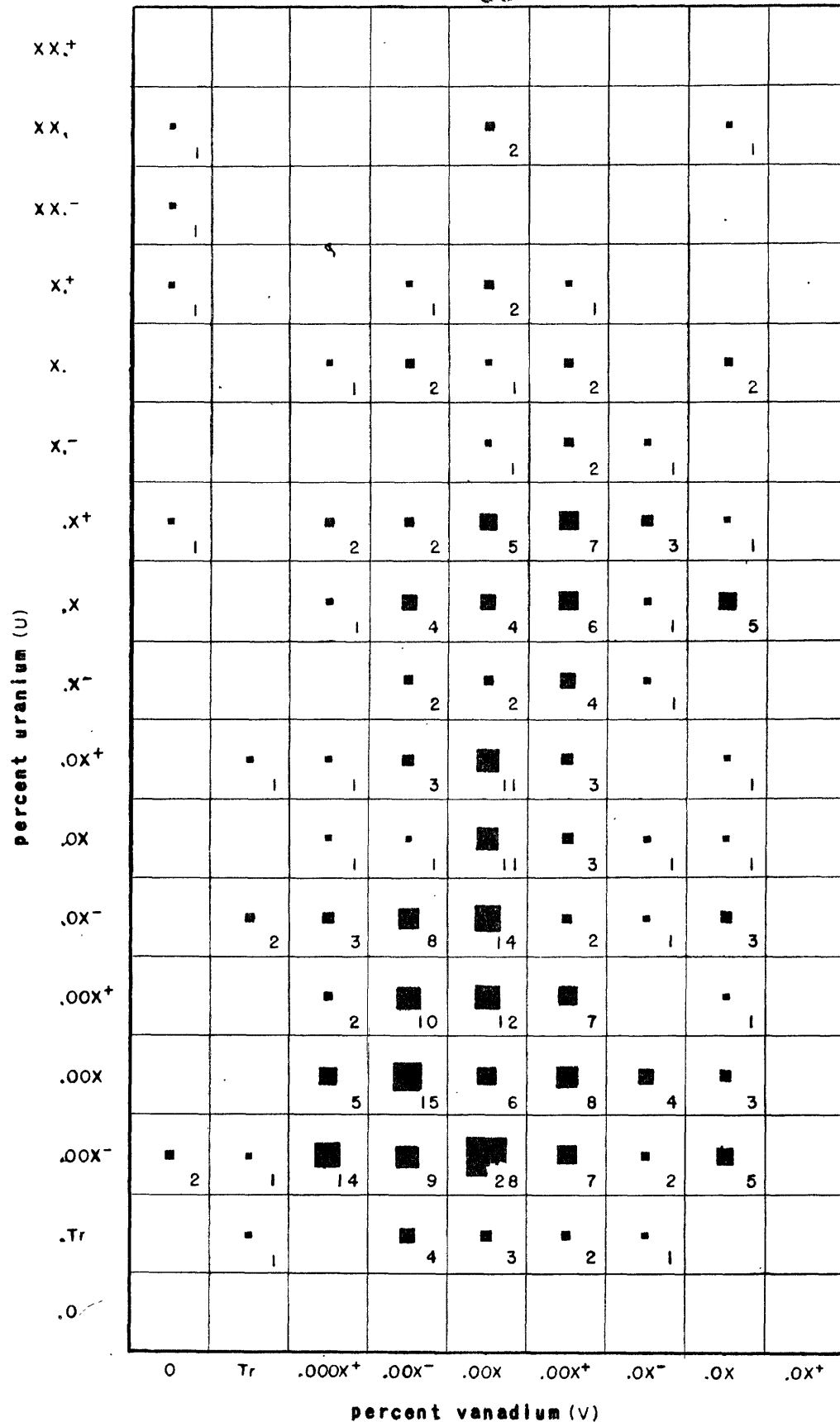taken by geologists of the Atomic Energy Commission and the Geological

Figure 1. Scatter diagram of geologic samples from uranium-bearing veins, showing the vanadium content plotted against uranium. The number of samples in each grade class is shown by the figure in the lower right corner of each square. The solid blocks, which are plotted as equivalent squares of the number of samples, also indicate visually the quantitative distribution of samples.

Survey during geologic study of uranium-bearing vein deposits. The samples are from 84 localities in 9 western states; some localities are represented by a single sample, others by a dozen or more samples. The localities represented were screened with care to include only those deposits that would be classed as hydrothermal veins; deposits for which there might be some reasonable doubt or argument regarding the hypogene source of the uranium are not represented in this group of samples. All available assay reports from these deposits were used. This group contains a few samples representing ore shipments or mill heads, but mostly they consist of grab or channel samples. As such, most individual samples cannot be considered as good samples of ore bodies, but collectively they may be broadly representative of this type of ore deposit--uranium-bearing vein deposits of hydrothermal origin.

All assays were made in the Denver Laboratory of the Geological Survey; only equivalent uranium determinations were made on samples having low radioactivity (a few thousandths percent eU), but chemical determinations for U were available for all other samples; all vanadium determinations were made by semiquantitative spectrographic analysis. For purposes of plotting on figure 1, the uranium assays (either eU or chemical U) were converted from the numerical figure to the grade classes used in reporting spectrographic results.

The frequency distribution of vanadium determinations in the several grade classes is tabulated on the right side of table 1. The samples are divided into two groups: one group consists of samples containing 0.01 percent or more U (column 4), as it was thought that this group might

be more representative of uranium-bearing ore bodies or ore shoots;

the other group consists of samples containing less than 0.01 percent

U (column 5). The combined totals for the two groups are shown in

column 6. The graphic plot below each column shows the distribution

of samples in each grade class by percent of the total number of samples.

The geometric mean for the combined total of samples (column 6,

table 1) is 31 ppm V, that for the samples containing 0.01 percent or

more U (column 4) is 36 ppm V, and that for the samples containing less

than 0.01 percent U (column 5) is 27 ppm V. These figures suggest a

slight tendency for vanadium to increase with an increase in uranium

content of these samples, but the difference in the mean

figures are so small that they might result from chance or random

variation in the sampling. The correlation coefficient between vanadium

and uranium for all samples (fig. 1) is +0.12, which is below the normal

level of significance.

The assay results of the group of 74 "ore samples" are plotted on

figure 2. This group includes samples taken for settlements on ore

shipments, samples of material used for metallurgical or pilot-plant

tests, and a few samples submitted by miners and prospectors. These

samples are from 36 localities (deposits) in 10 western states and 4

foreign countries; some localities are represented by single samples,

others by several samples; a few samples represent average assays calcu-

lated for numerous shipments of ore from a single mine. As such, most

of the samples are presumably well representative of ore and the parent

ore bodies, and from this standpoint they are better than those classed

2.15

1.0

.464

.215

percent uranium (U)

.10

.0464

.0215

.010

2

13

13

17

4

6

2

1

4

1

2

1

2

1

Sample contains
20.1 percent TiO_2

Sample contains
35.0 percent TiO_2

Sample contains
4.7 percent TiO_2

Sample is Ti-bearing
but the amount is
not reported

1

1

1

1

1

less .01
than
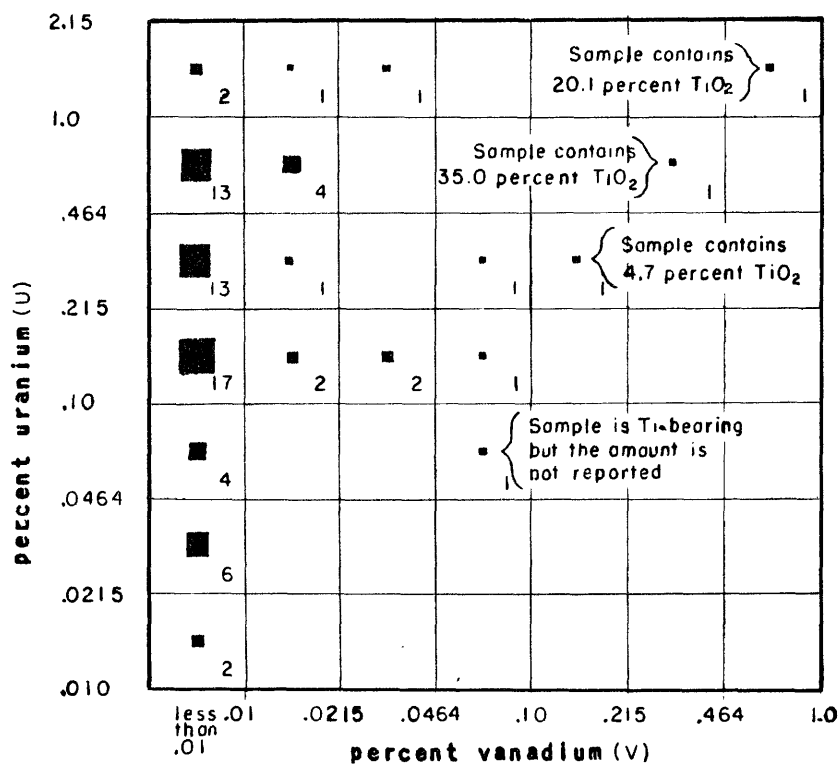.01   .0215   .0464   .10   .215   .464   1.0

percent vanadium (V)

Figure 2. Scatter diagram of uranium ore samples, showing the vanadium
content plotted against uranium. The number of samples in each grade
class is shown by the figure in the lower right corner of each square.
The solid blocks, which are plotted as equivalent squares of the number
of samples, also indicate visually the quantitative distribution of samples.

as geologic samples. All assays were made by chemical methods, mostly
of the routine "commercial" type, and by several laboratories. With
these methods the threshold of determination for vanadium is in the low
hundredths percent V_2O_5, and assay accuracy at this level is admittedly
poor. Discrepancies ranging from 0.01 to 0.04 percent V_2O_5 have been
noted between different laboratories and different standards of analyses.
At this low level of vanadium content, such discrepancies, of course, are
of no practical concern to the ore vendor, buyer, or metallurgist, but
they do present problems in a study of this kind. Futhermore, many of
the vanadium determinations in this group of samples are reported as "0.00
percent V_2O_5" or as "<0.01 percent V_2O_5." When converted to V for plotting
on figure 1, these values are all plotted in the vanadium grade class of
"less than 0.01."

Because the accuracy of the vanadium assays for these ore samples is
subject to question, it is difficult to determine whether or not the
relations shown by figure 2 have any true significance. The illustration
is presented, however, so the reader can see these data and arrive at his
own conclusions. It is obvious that the higher grade vanadium samples
occur with some of the higher grade uranium samples and none of the low-
grade uranium samples contain much vanadium. Even so, the vanadium content
of all these samples is quite low, except those containing abundant titanium.

Because of the vanadium-titanium relations shown on figure 2 and
the association suggested by the study of the ores and mill-products
samples (p. 20), a record was made of the spectrographic determinations
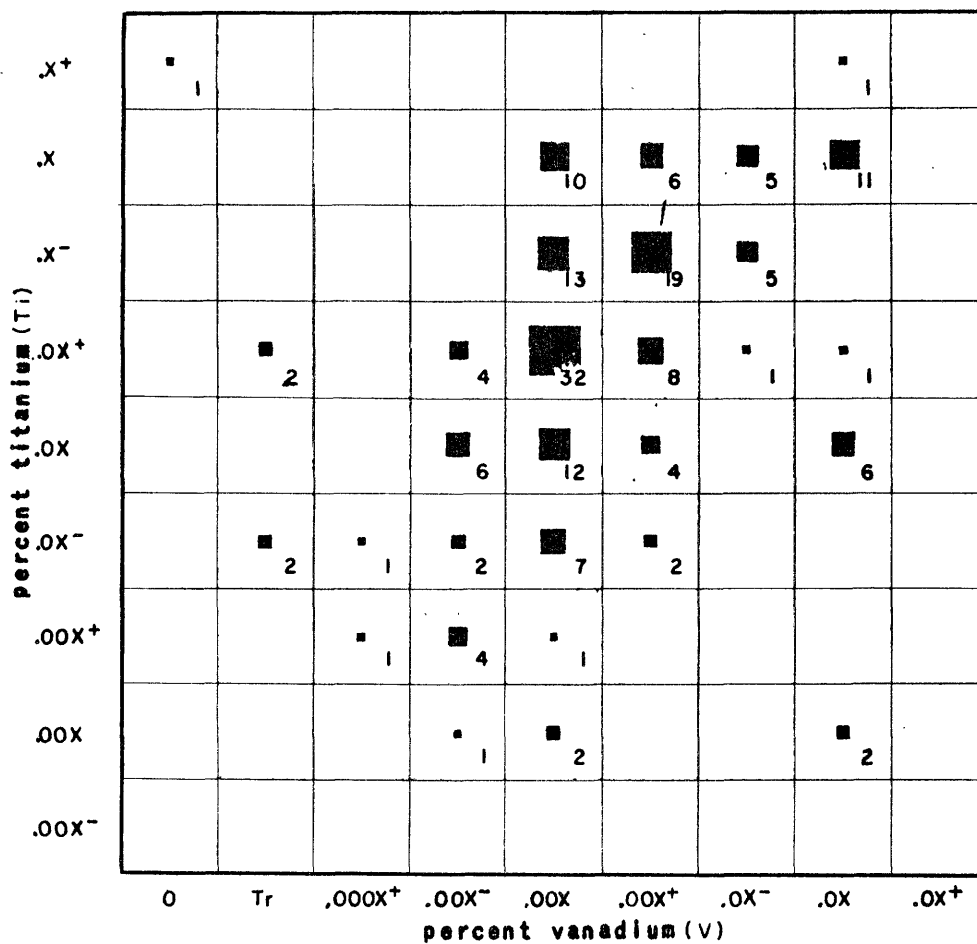of titanium for 172 of the 296 samples of uranium-bearing veins. Figure 3

Figure 3. Scatter diagram of samples from uranium-bearing veins, showing the vanadium content plotted against titanium. The number of samples in each grade class is shown by the figure in the lower right corner of each square. The solid blocks, which are plotted as equivalent squares of the number of samples, also indicate visually the quantitative distribution of samples.

is a scatter diagram showing the vanadium content of these 172 samples

plotted against titanium. The correlation coefficient between vanadium

and uranium in these samples is +0.36, which is low but significant.

Presumably none of these samples are from deposits in which titanium

is much enriched, for the titanium content of most samples, as well as

their vanadium content, is that common among rocks. Likely the titanium

and vanadium in these samples is essentially the same as the content of

these metals in the host rocks of these deposits.

Wright (1954) arrived at a similar conclusion regarding vanadium

and titanium in his study of a uraninite deposit at Caribou, Colo. He

tested the vein at three places with sets of samples from the host rock

through the altered zones on both sides of the vein; spectrographic

determinations showed the titanium content to be constant at 0.1 to 1.0

percent and the vanadium content at 0.01 to 0.1 percent (Wright, 1954,

figs. 3, 4, and 5). In an unpublished report to the Atomic Energy

Commission he states, "this distribution indicates that the titanium

and vanadium present in the altered wall rock were original constituents

of the monzonite and were not supplied by the vein; and that leaching

of these elements by vein solutions was negligible."

The information plotted on figures 1 and 2, and tabulated on the

right side of table 1, permit a few broad generalizations. For the

deposits represented by the samples used in this study it appears that

vanadium is concentrated in large amounts only in uranium-bearing veins

containing abundant titanium. The average vanadium content in the other

deposits is probably no more, and perhaps is somewhat less, than the

average vanadium content of most rocks at the earth's crust, as reported by Rankama and Sahama (1950) and by others. This suggests that there is little or no tendency for vanadium to concentrate with uranium in most hydrothermal uranium-bearing veins. Nevertheless, the tabulation of these assays do show a slight tendency for vanadium to increase in amount with an increase in uranium.

In addition to generalizations made above, a few more detailed observations made during the compilation of these data seem worthy of record.

The assays of several uraninite or pitchblende specimens or concentrates were found; these, however, were not included with the other samples, because of the peculiar character of the sample or the manner in which the assay was reported. The vanadium content of these samples was reported to range from zero to a few tenths percent V_2O_5. Among these several samples there is a slight suggestion that the vanadium content may be higher in "sooty pitchblende" than in crystalline uraninite. Geologists working on uranium-bearing veins may be interested in checking this suggestion.

Among groups of samples from most uranium-bearing veins there is no obvious tendency for the vanadium content to increase with the uranium content. Exceptions to this generalization were noted in samples. from the Schwartzwalder mine, Jefferson County, Colo., and the Miracle mine, Kern County, Calif. In both deposits the vanadium content is moderately high (perhaps averaging 0.1 to 0.2 percent V_2O_5)─/, and in the available samples from both deposits there is an obvious, though not an

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─/ A composite of sample pulps representing more than 400 tons of ore shipped from the Schwartzwalder mine shows only .0X- percent V, spectrographically. This analysis was received after the tabulation of all the other data used in this report.

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invariable, tendency for vanadium to increase with uranium. The writer has no idea why these two deposits have a moderately abnormal vanadium content. Titanium is not obviously concentrated in the Schwartzwalder deposit; the writer has no data regarding the titanium content of the ore from the Miracle mine.

VANADIUM IN HOT SPRINGS

Like the geologic descriptions of most ore deposits, reports on hot springs and hot-spring sediments usually fail to mention vanadium. The assumption can be made that vanadium is not abundant in these thermal solutions and that it does not precipitate from them in recognizable minerals--but this is negative evidence and weak.

Based on his studies of hot-spring waters and sediments at Steamboat Springs, Nev., and Morgan Springs and Wilbur Springs, Calif., D. E. White (written communication) states:

"Vanadium is not present in amounts detectable by spectrographic methods in the dissolved solids of water samples from Steamboat Springs, Nev., and Morgan Springs and Wilbur Springs, Calif. Its content in the water at Steamboat Springs is less than 0.2 ppm and less than 2 ppm in the highly saline water of Wilbur Springs.

"On the other hand, several samples of sediments from these three springs showed 0.0X percent V by spectrographic analysis, and two from Steamboat Springs showed 0.01 percent V_2O_3 by gravimetric analysis.

"Vanadium is not being deposited within the explored depths of the Steamboat Springs system, and there is even some evidence pointing toward a slight leaching of vanadium from the wall rock by the hydrothermal solutions.

"Hot springs have not yet thrown light on the origin of hypogene uranium deposits. Hot spring waters are lower in uranium content than many other types of waters."

SUMMARY AND CONCLUSIONS

Vanadium and uranium are dispersed in igneous rocks, but the two metals are not intimately associated in this environment--vanadium is more abundant in the mafic rocks, uranium in the silicic ones.

Both metals tend to concentrate in some sedimentary rocks, especially those containing organic material; in these rocks either metal alone may be enriched or both together.

Uranium obviously enters the hydrothermal environment, and in places it concentrates sufficiently in veins to form commercially valuable deposits. Prospecting in recent years has shown that uranium is rather widely distributed in hydrothermal veins.

None of the productive vanadium deposits, on the other hand, are of undoubted hydrothermal origin, although the vanadate ores and the deposit at Minasragra do have some characteristics of hydrothermal deposits. Furthermore, except in some titanium-bearing veins and some gold or gold-telluride deposits, vanadium-bearing minerals have not been generally recognized in hydrothermal deposits, suggesting a low-vanadium content in most hydrothermal deposits, a suggestion that seems to be confirmed by recently available spectrographic data. A group of 775 analyses of samples of ores and mill products from numerous deposits in the United States shows an average of less than 100 ppm V, a content somewhat less

than that commonly reported for igneous rocks and shale. A second

group of 296 samples from uranium-bearing veins also shows an average

of less than 100 ppm V. Perhaps the vanadium in many of these samples

is that of the wall rock rather than introduced vanadium.

Although these samples certainly do not give a complete coverage

of ore deposits, and many individual samples certainly are not rep-

resentative of their parent ore bodies, as a group they probably represent

the best available sample of vanadium in ore deposits in general and in

uranium-bearing veins in particular. They suggest that vanadium does

not tend to concentrate in the common hydrothermal environment, and spe-

cifically that it does not concentrate in most veins containing uranium

ore. If this is true, it appears that deposits containing commercial

amounts of both vanadium and uranium, such as deposits of the sandstone

type, are not common hydrothermal deposits.

The fact that both vanadium and uranium do accumulate in some sedi-

mentary rocks containing organic material suggests that a thorough study

be made of the geochemical processes that influence this accumulation,

to see if in any way these processes are compatible with the geologic

habits of the productive vanadium-uranium deposits of the sandstone type,

most of which do contain plant fossils.

The lack of evidence that vanadium and uranium are enriched together

in common hydrothermal deposits does not eliminate the possibility that

in the sandstone deposits these metals had a hypogene origin and were

formed by hydrothermal processes. However, it would seem to require field

evidence that unusual processes or conditions were extant in order to

support the idea of deposition from hot ascending aqueous solutions.

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